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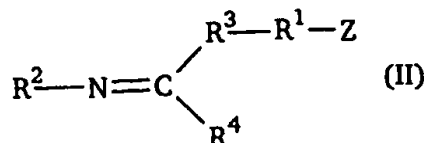
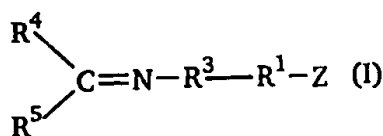
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(54) Title: MODIFIED POLYMERS PREPARED WITH LANTHANIDE-BASED CATALYSTS



(57) Abstract: A method for preparing a functionalized polymer comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated diene monomer with a lanthanide-based catalysts, and reacting the pseudo-living polymer with at least one functionalizing agent defined by the formula (I) or (II) where Z is a substituent that will react or interact with organic or inorganic fillers; R<sup>1</sup> is a single bond or a divalent organic group; R<sup>2</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>3</sup> or R<sup>4</sup>; R<sup>3</sup> is a single bond, a divalent organic group, or a trivalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup>; R<sup>4</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>5</sup>; R<sup>5</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup>; and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Z are substituents that will not protonate pseudo-living polymer. Also vulcanizable compositions containing functionalized polymers having filler-interactive substituents that are useful in the production of tires and other industrial products.

WO 01/34659 A1

## **MODIFIED POLYMERS PREPARED WITH LANTHANIDE-BASED CATALYSTS**

This application gains priority from U.S. Patent Application Serial No. 60/165,169, filed November 12, 1999.

### **FIELD OF THE INVENTION**

This invention relates to functionalized polymers and processes for functionalizing these polymers. More particularly, these functionalized polymers are prepared with a lanthanide-based catalyst systems and reacted with a functionalizing agent comprising an imine group and a filler-interactive group.

### **BACKGROUND OF THE INVENTION**

Conjugated diene polymers are commonly used in the rubber industry. These polymers are often prepared by using coordination-catalysis techniques because the microstructure of the resulting polymer can be controlled. Polybutadiene having greater than 90 percent of its units in the 1,4-*cis* configuration can be produced with a coordination catalyst system that includes a nickel, cobalt, or titanium compound, an alkylating agent, and a halogen source. Polymers having this microstructure have a low glass transition temperature ( $T_g$ ), which provides good low-temperature properties. Also, high 1,4-*cis* polymers have excellent wear resistance and mechanical properties such as reduced cut growth.

The tire industry has been challenged to design tires that have improved rolling resistance, which contributes to better fuel efficiency. Attempts to improve rolling resistance have included alternate tire designs and the use of rubber that has less hysteresis loss. Also, there has been a general trend toward the use of silica as a reinforcing filler. Polymers that interact with the reinforcing fillers of tires have demonstrated less hysteresis loss.

Functionalized polymers prepared with anionic polymerization techniques have demonstrated lower hysteresis loss. They can be functionalized both at initiation and termination. Polybutadiene has been produced by initiating polymerization of 1,3-butadiene with functionalized initiators to provide polymers that have a greater affinity toward carbon black or silica fillers. Anionically polymerized polymers have also been terminated with functionalized terminators

to provide polymers that have a greater affinity toward carbon black or silica fillers. Unfortunately, because anionic polymerization does not provide strict control over the polymer microstructure, high 1,4-*cis* polymers are not obtained.

Coordination catalysis limits the ability to functionalize the resulting  
 5 polymers because they operate by chemical mechanisms that involve the interaction of several chemical constituents, and often also involve self-termination reactions. As a result, the reaction conditions required to achieve functionalization are difficult to obtain.

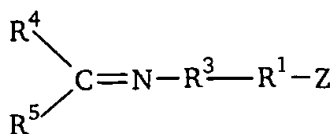
Terminating agents, such as organo metal halides, heterocumulene  
 10 compounds, three-membered heterocyclic compounds, and certain other halogen containing compounds, will react with polymers prepared with a lanthanide-based catalyst system. The resulting functionalized polymers, however, do not have a useful enough affinity toward either organic or inorganic fillers.

Therefore, there is a need in the art to provide functionalizing agents  
 15 that will react with polymers prepared with coordination catalysts to yield functionalized polymers having a high *cis* microstructure and an affinity toward carbon black and silica.

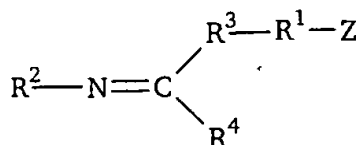
### SUMMARY OF THE INVENTION

20 In general the present invention provides a method for preparing a functionalized polymer comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated diene monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with at least one functionalizing agent defined by the formula (I) or (II)

25



(I)



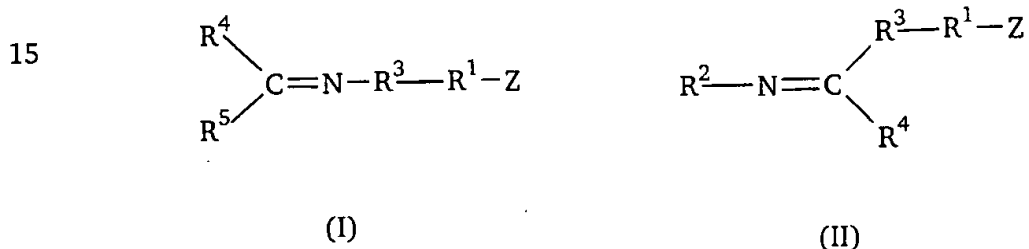
(II)

30

where Z is a substituent that will react or interact with organic or inorganic fillers; R<sup>1</sup> is a single bond or a divalent organic group; R<sup>2</sup> is a monovalent organic group

or a divalent organic group that forms a cyclic organic group with R<sup>3</sup> or R<sup>4</sup>; R<sup>3</sup> is a single bond, a divalent organic group, or a trivalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup>; R<sup>4</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>5</sup>; R<sup>5</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup>; with the proviso that each group attached to the imino carbon is attached via a carbon atom and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Z are substituents that will not protonate a pseudo-living polymer.

The present invention also includes a functionalized polymer prepared by a process comprising the steps of preparing a pseudo-living polymer by polymerizing conjugated monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with a functionalizing agent defined by the formula (I) or (II)

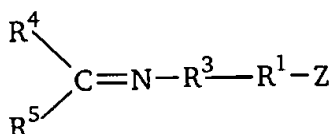


where Z is a substituent that will react or interact with organic or inorganic fillers; R<sup>1</sup> is a single bond or a divalent organic group; R<sup>2</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>3</sup> or R<sup>4</sup>; R<sup>3</sup> is a single bond, a divalent organic group, or a trivalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup>; R<sup>4</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>5</sup>; R<sup>5</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup>; with the proviso that each group attached to the imino carbon is attached via a carbon atom and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Z are substituents that will not protonate a pseudo-living polymer.

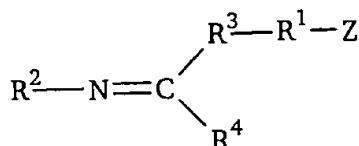
The present invention further includes a vulcanizable composition of matter comprising (a) a rubber component comprising a functionalized polymer prepared by a process comprising the steps of preparing a pseudo-living polymer

by polymerizing conjugated monomer with a lanthanide-based catalyst, and reacting the pseudo-living polymer with a functionalizing agent defined by the formula (I) or (II)

5



(I)



(II)

10 where Z is a substituent that will react or interact with organic or inorganic fillers; R<sup>1</sup> is a single bond or a divalent organic group; R<sup>2</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>3</sup> or R<sup>4</sup>; R<sup>3</sup> is a single bond, a divalent organic group, or a trivalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup>; R<sup>4</sup> is a monovalent organic group or a  
15 divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>5</sup>; R<sup>5</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup>; with the proviso that each group attached to the imino carbon is attached via a carbon atom and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Z are substituents that will not protonate a pseudo-living polymer, and (b) a reinforcing filler.

20 It has now been found that polymers prepared with lanthanide-based catalysts can be functionalized with certain functionalizing agents to produce functionalized polymers that are technologically useful.

### DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

25 The present invention is directed toward novel functionalizing agents, a process for functionalizing polymers prepared with lanthanide-based catalysts, the resulting functionalized polymers, and the use of these functionalized polymers within tires.

30 The polymers that are functionalized are prepared from lanthanide-based coordination catalyst systems. These polymers are preferably characterized in that greater than about 85 percent of the polymer is in the *cis* microstructure, less than about 3% of the polymer is in the 1,2- or 3,4- microstructure, and

molecular weight distribution of the polymer is less than about 4. Because these polymers have been found to demonstrate some living characteristics, they may be called pseudo-living polymers within this specification.

This invention is not limited to functionalizing a polymer prepared from  
5 any particular lanthanide-based catalyst. One useful catalyst includes a lanthanide compound, an alkylating agent, and a source of halogen. The lanthanide compound can include neodymium (Nd) carboxylates including Nd neodecanoate. Also, the lanthanide compound can include the reaction product of a Nd carboxylate and a Lewis base such as acetylacetone. The alkylating agents can  
10 generally be defined by the formula  $AlR_3$ , where each R, which may be the same or different, is hydrogen, a hydrocarbyl group, or an alkyl aluminoxy group, with the proviso that at least one R is a hydrocarbyl group. Examples of these alkylating agents include, but are not limited to, trialkyl aluminum, dialkyl aluminum hydride, alkyl aluminum dihydride, and mixtures thereof. Examples of alkylating  
15 agents where R is an alkyl aluminoxy group include methyl aluminoxanes. Sources of halogen can include organoaluminum chloride compounds. Catalyst systems that generally include lanthanide compounds and alkylating agents definable by the formula  $AlR_3$  are disclosed in U.S. Pat. Nos. 3,297,667, 3,541,063, and 3,794,604, which are incorporated herein by reference.

20 One particularly preferred catalyst includes (a) the reaction product of Nd carboxylate and acetylacetone, (b) triisobutylaluminum, diisobutylaluminum hydride, isobutylaluminum dihydride, or a mixture thereof, and (c) diethylaluminum chloride, ethylaluminum dichloride, or mixtures thereof. This catalyst system is disclosed in U.S. Pat. No. 4,461,883, which is incorporated  
25 herein by reference. Another preferred catalyst includes (a) Nd neodecanoate, (b) triisobutylaluminum, diisobutylaluminum hydride, isobutylaluminum dihydride, or a mixture thereof, and (c) diethylaluminum chloride, ethylaluminum dichloride, or mixtures thereof. This catalyst system is disclosed in Can. Pat. No. 1,223,396, which is incorporated herein by reference.

30 Still another preferred lanthanide-based catalyst system includes (a) a lanthanide compound such as Nd carboxylate, (b) an aluminoxane such as methyl aluminoxane, which may optionally be used in conjunction with an alkylating

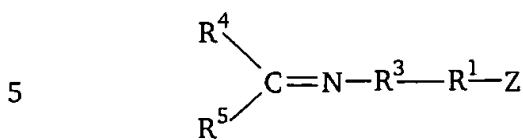
agent such as diisobutylaluminum hydride, and (c) a source of halogen such as diethylaluminum chloride. Neodymium catalysts that include alkyl aluminoxane compounds are described in Japanese Kokai publications 06-211916, 08-073515, 10-306113, and 11-035633, which are incorporated herein by reference. In an especially preferred embodiment of the system with aluminoxanes, the source of halogen is a metal halide of Group I, II, or VII metals. These metal halides include, but are not limited to, BeCl<sub>2</sub>, BeBr<sub>2</sub>, BeI<sub>2</sub>, MgCl<sub>2</sub>, MgBr<sub>2</sub>, MgI<sub>2</sub>, CaCl<sub>2</sub>, CaBr<sub>2</sub>, CaI<sub>2</sub>, BaCl<sub>2</sub>, BaBr<sub>2</sub>, BaI<sub>2</sub>, ZnCl<sub>2</sub>, ZnBr<sub>2</sub>, ZnI<sub>2</sub>, CdCl<sub>2</sub>, HgCl<sub>2</sub>, MnCl<sub>2</sub>, ReCl<sub>2</sub>, CuCl<sub>2</sub>, AgCl<sub>2</sub>, AuCl. Other lanthanide-based catalysts and processes for their use are described in U.S. Patent Nos. 4,444,903, 4,525,549, 4,699,960, 5,017,539, 5,428,119, 5,064,910, and 5,844,050, which are incorporated herein by reference.

Typically, from about 0.0001 to about 1.0 mmol of lanthanide metal are employed per 100 grams of monomer. More preferably, from about 0.001 to about 0.75, and even more preferably from about 0.005 to about 0.5 mmol of lanthanide metal per 100 grams of monomer are employed. The ratio of alkylating agent to lanthanide metal is from about 1:1 to about 1:500, more preferably from about 3:1 to about 250:1, and even more preferably from about 5:1 to about 200:1. The ratio of halogen source to lanthanide metal is from about 0.1:1 to about 30:1, more preferably from about 0.2:1 to about 15:1, and even more preferably from about 1:1 to about 10:1.

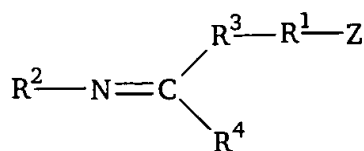
Monomers that are polymerized by the lanthanide-based catalysts are conjugated diene monomers that include, but are not limited to, 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, and myrcene. 1,3-butadiene is most preferred. These conjugated dienes may be used either alone or in combination. If desired, a small amount of monomer other than conjugated dienes can be added. These other monomers include, but are not limited to, aromatic 1,2- or 3,4- compounds such as styrene. The amount of the copolymerizable monomer is not limited, but is usually less than 10 percent by weight, preferably less than 5 percent by weight, and even more preferably less than about 3 percent by weight of the entire polymer.

According to this invention, pseudo-living polymers prepared with lanthanide-based catalysts are reacted with certain functionalizing agents to

produce terminally-functionalized polymers. Useful functionalizing agents include imine containing compounds defined by formulas (I) and (II)



(I)



(II)

10 where Z is a filler-interactive substituent that will react with or interact with organic or inorganic fillers, R<sup>1</sup> is a single bond or a divalent organic group, R<sup>2</sup> is a monovalent organic group, R<sup>3</sup> is a single bond or a divalent organic group, R<sup>4</sup> is a hydrogen atom, an amino group, or a monovalent organic group, and R<sup>5</sup> is a monovalent organic group, with the proviso that at least one of R<sup>4</sup> or R<sup>5</sup> in  
 15 formula (I) is attached to the imine carbon via a carbon atom, and where R<sup>3</sup> in formula (II) is attached to the imine carbon via a carbon atom. R<sup>3</sup> may combine with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup> to form a cyclic organic group, or R<sup>2</sup> may combine with R<sup>4</sup> to form a cyclic organic group. Consequently, R<sup>3</sup> may be a trivalent organic group and R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup> may be divalent organic groups. R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> are  
 20 substituents that will not protonate a pseudo-living polymer. As used throughout this specification, substituents that will not protonate a pseudo-living polymer refer to those substituents that will not donate a proton to the polymer in a protolysis reaction.

25 Preferably, the divalent organic groups are hydrocarbylene groups that contain from 1 to about 20 carbon atoms. More preferably, these hydrocarbylene groups will contain from about 1 to about 10 carbon atoms, and even more preferably from about 2 to about 8 carbon atoms. These hydrocarbylene groups include aliphatic, cycloaliphatic, and aromatic groups including, but not limited to, alkylene, cycloalkylene, substituted alkylene, substituted cycloalkylene, alkenylene, cycloalkenylene, substituted alkenylene, substituted cycloalkenylene, arylene, and  
 30 substituted arylene. The term "substituted" refers to an organic group, such as a hydrocarbyl group, that replaces a hydrogen atom attached to a carbon within the



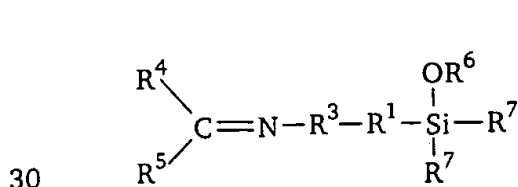
group. The hydrocarbylene groups may contain hetero atoms including nitrogen (N), oxygen (O), sulfur (S), phosphorous (P), and silicon (Si). When these hydrocarbylene groups include O, they may be referred to as oxo-hydrocarbylene groups, and where they include N, they may be referred to as aza-hydrocarbyl-  
 5 hydrocarbylene groups.

Some specific examples of hydrocarbylene groups include methylene, ethylene, 1,3-propylene, 1,2-propylene, 1,4-butylene, 1,4-(2-methyl)butylene, 1,5-pentylene, cyclopentylene, phenylene, and 1-(aza-hydrocarbyl)hydrocarbylene.

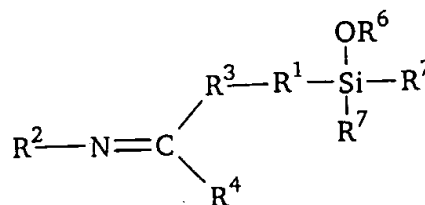
Preferably, the monovalent organic groups are hydrocarbyl groups that  
 10 contain from 1 to about 20 carbon atoms. More preferably, these groups include from about 2 to about 10 carbon atoms, and even more preferably from about 3 to about 8 carbon atoms. These hydrocarbyl groups can include, but are not limited to, alkyl, cycloalkyl, substituted alkyl, substituted cycloalkyl, alkenyl, cycloalkenyl, substituted alkenyl, substituted cycloalkenyl, aryl substituted aryl,  
 15 allyl, aralkyl, alkaryl, and alkynyl and may contain hetero atoms including, but not limited to, N, O, S, P, and Si. When these hydrocarbyl groups include O, they may be referred to as oxo-hydrocarbyl groups, and where they include N, they may be referred to as aza-hydrocarbyl-hydrocarbyl groups. Some specific examples of hydrocarbyl groups include methyl, ethyl, propyl, isopropyl, butyl, 2-methylbutyl,  
 20 pentyl, hexyl, cyclohexyl, heptyl, octyl, cyclo-octyl, 2-ethylhexyl, 2-propylhexyl, and 1-(aza-hydrocarbyl)hydrocarbyl groups.

Non-limiting examples of imine groups include benzilidene hydrocarbyl amine, N-hydrocarbyl diaryl ketimine,  $\alpha,\alpha$ -substituted alkylene aryl amine.

In one particular embodiment, where the filler-interactive group Z  
 25 contains a silane group such as triethoxysilylpropyl, the functionalizing agents are be defined by the formulas (III) and (IV)



(III)



(IV)

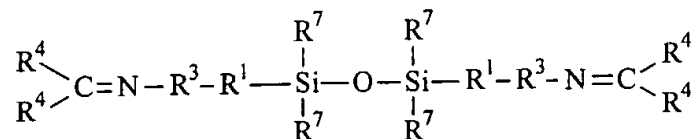
where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> are as defined above, R<sup>6</sup> is a monovalent organic group, and each R<sup>7</sup>, which may be the same or different, is a monovalent organic group or a substituent defined by -OR<sup>8</sup>, where R<sup>8</sup> is a monovalent organic group. R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are substituents that will not protonate a pseudo-  
 5 living polymer. Preferably, at least one R<sup>7</sup> is -OR<sup>8</sup>, and even more preferably each R<sup>7</sup> is -OR<sup>8</sup>. The monovalent organic groups are preferably hydrocarbyl groups that contain from 1 to about 20 carbon atoms, more preferably from about 2 to about 10 carbon atoms, and even more preferably from 3 to about 8 carbon atoms.

Specific non-limiting examples of compounds definable by the formulas  
 10 (III) and (IV) include N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (TEOSI) and N-(1,3-dimethylbutylidene)-3-triethoxysilyl)-1-propaneamine (HAPEOS).

Those skilled in the art will be able to readily synthesize the silane-containing compounds defined by the formulas (II) and (IV). For example, ketones or aldehydes may be reacted with an amine that contains a carbon-carbon double bond, and the reaction product thereof may be reacted with an alkoxy silicon  
 15 hydride via hydrosilation.

Dimers, trimers, or even larger oligomers of alkoxy silane compounds can also be employed. For example, a dimer of compounds represented by the formula (III) can be represented by the following formula (V)

20



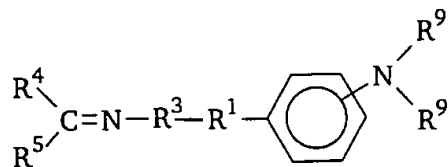
(V)

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Because functionalizing agents containing alkoxy silane filler-interactive groups are likely to oligomerize, reference to these compounds will likewise refer to oligomers thereof.

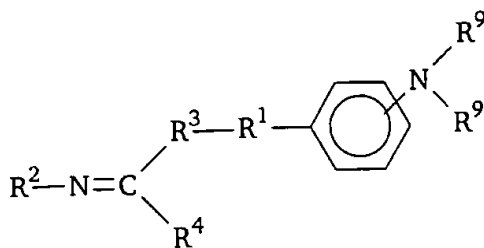
In another embodiment, where the filler-interactive group Z contains a  
 30 N,N-disubstituted amino phenyl group, functionalizing agents of the present invention are defined by the formulas (VI) and (VII)

10



5

(VI)



10

(VII)

15

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  are as defined above, and where each  $\text{R}^9$ , which may be the same or different, is a monovalent organic group or amino group, with the proviso that  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ , and  $\text{R}^9$  are substituents that will not protonate a pseudo-living polymer. The monovalent organic groups preferably contain from 1 to about 20 carbon atoms. More preferably, these groups will include from about 2 to about 10 carbon atoms, and even more preferably from about 3 to about 8 carbon atoms.

Non-limiting examples of N,N-disubstituted amino phenyl groups include N,N-diethylaminophenyl, N,N-dimethylaminophenyl, hexamethyleneimin-N-o-phenyl, pyrrolidin-1-o-phenyl.

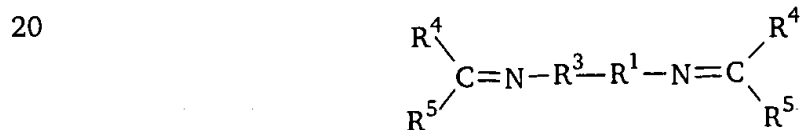
Non-limiting examples of compounds that are generally definable by the formulas (VI) and (VII) include dialkylaminobenzylidene alkylamines such as dimethylaminobenzylidene ethylamine, diethylaminobenzylidene -butylamine; dialkylaminobenzylidene anilines such as dimethylaminobenzylidene aniline, dimethylaminobenzylidene n-butyraniline (DMAB-BPA),

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dimethylaminobenzylidene dodecylaniline, dimethylaminobenzylidene methoxyaniline, dimethylaminobenzylidene dimethylaminoaniline; bis(dialkylaminophenyl)methylidene alkylamines such as bis(dimethylaminophenyl)methylidene -butylamine, 5 bis(dimethylaminophenyl)methylidene n-octylamine, bis(diethylaminophenyl)methylidene -butylamine, bis(diethylaminophenyl)methylidene n-octylamine; benzylidene dialkylaminoanilines such as benzylidene dimethylaminoaniline, methoxybenzylidene dimethylaminoaniline, alpha,alpha-disubstituted alkylidene 10 dialkylaminoaniline such as 1-methyl-4-pentene-2-yl-methylidene dimethylaniline, or other alkylidene dialkylaminoanilines such as 1,3-dimethylbutylidene dimethylaniline. Many other compounds are disclosed in U.S. Patent No. 5,066,729, which is incorporated herein by reference.

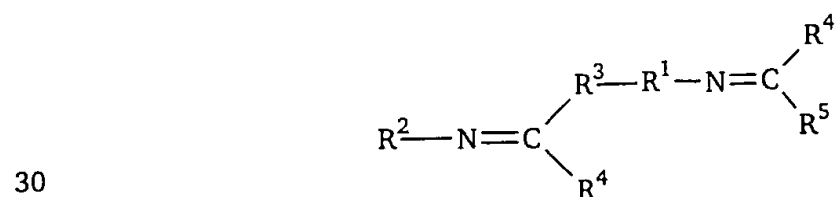
Those skilled in the art will be able to readily synthesize the N,N- 15 disubstituted amino phenyl-containing compounds defined by the formulas (VI) and (VII). Also, their synthesis is described in U.S. Patent No. 5,153,159.

In another embodiment, where the filler-interactive group Z contains an imine group, the functionalizing agent can be defined by the formulas (VIII), (IX), and (X)

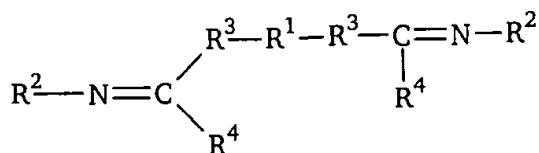


(VIII)

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(IX)



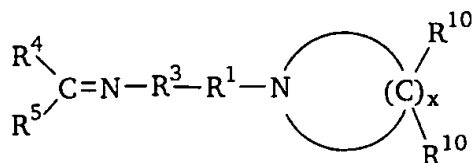
(X)

where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> are as defined above, with the proviso that at least one of R<sup>4</sup> or R<sup>5</sup> in formulas (VIII) and (XI) is attached to the imine carbon via a carbon atom. R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>10</sup> are substituents that will not protonate a pseudo-living polymer.

Non-limiting examples of imine groups include alkylene amines, benzylideneamines, and imidazoles including N-(4,5-dihydroimidazole) groups. Non-limiting examples of compounds that are generally definable by the formulas (VIII), (IX), and (X) include phenylene bis(dimethylaminobenzylidene amine).

Those skilled in the art will be able to readily synthesize the imine-containing compounds defined by the formulas (VIII), (IX) and (X). For example, the compounds defined by the formula (VIII) may be prepared by reacting a diamine with desired ketone or aldehyde compound.

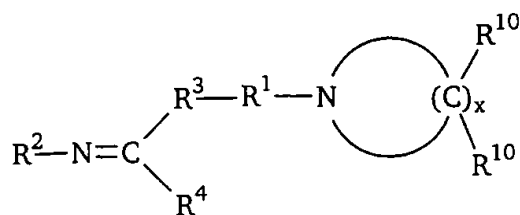
20 In another embodiment, where the filler-interactive group Z contains a cyclic amino group, the functionalizing agents can be defined by the formulas (XI) and (XII)



(XI)

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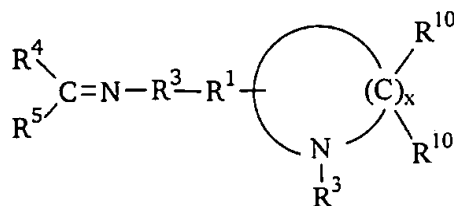
(XII)

10 where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>10</sup> are as defined above, where two R<sup>10</sup> groups can join to form a bicyclo structure, and x is an integer from 4 to about 20. In forming the bicyclo structure, two R<sup>10</sup> groups attached to the same carbon atom may join or, in alternatively, R<sup>10</sup> groups on separate ring carbons may join to form a bicyclo group. R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>10</sup> are substituents that will not  
 15 protonate a pseudo-living polymer.

Non-limiting examples of cyclic amino groups include 1-hexamethyleneimino, 1-pyrrolidino, 1-piperidino, 1-dodecamethyleneimino, and 4-substituted 1-piperazino groups. Non-limiting examples of compounds that are generally definable by the formulas (XI) and (XII) include benzylidene (1-hexamethyleneimino)aniline, benzylidene (1-pyrrolidino)aniline,  
 20 dimethylaminobenzylidene (1-hexamethyleneimino)aniline, dimethylaminobenzylidene (1-pyrrolidino)aniline, (1-hexamethyleneimino)benzylidene aniline, and (1-pyrrolidino)benzylidene aniline.

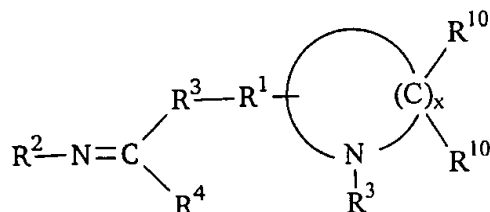
In another embodiment where the filler-interactive group Z contains a  
 25 cyclic amino group, the functionalizing agents can be defined by the formulas (XIII) and (XIV)

30



(XIII)

5



(XIV)

10 where  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^{10}$  and  $x$  are as defined above. The cyclic amino group can include heteroatoms within the cyclic ring. In other words, the carbon atom designated C can be replaced by O, N, S, Si, or P.

A non-limiting example of cyclic amino groups includes 3-(1-methyl)pyrolidino group. Non-limiting examples of compounds that are definable  
 15 by the formulas (XIII) and (XIV) include benzylidene 4-(1-n-butyl piperazino)-methyl aniline, benzylidene ((3-(1-methyl)pyrolidino)methyl)aniline, 4-(4-(1-n-butyl)piperazino)methyl benzylidene aniline, 4-((3-(1-methyl)pyrolidino)methyl)benzylidene aniline.

Those skilled in the art will be able to readily synthesize the cyclic  
 20 amino-containing compounds defined by the formulas (XI), (XII), (XIII) and (XIV). For example, a cyclic amine-containing primary amine can be reacted with a desired ketone or aldehyde.

Epoxy compounds that will not protonate a pseudo-living polymer can be used in combination with the foregoing functionalizing agents to react with  
 25 pseudo-living polymers to form blends of functionalized polymers. These epoxy compounds include, but are not limited to, styrene oxide, epoxydized soy bean oil, glycidyl (meth)acrylate, diglycidyl ether, ethylene oxide, propylene oxide, 1,2-epoxybutane, 1,2-epoxyisobutane, 2,3-epoxybutane, 1,2-epoxyhexane, 1,2-epoxyoctadecane, 1,2-epoxyeicosane, 1,2-epoxy-2-pentylpropane, 3,4-epoxy-1-butene, 1,2-epoxy-5-hexene, 1,2-epoxy-9-decene, 1,2-epoxycyclopentane, 1,2-epoxycyclohexane, 1,2-epoxycyclododecane, 1,2-epoxyethylbenzene, 1,2-epoxy-1-methoxy-2-methylpropane, glycidyl methyl ether, glycidyl ethyl ether, glycidyl  
 30

isopropyl ether, glycidyl phenyl ether, glycidyl butyl ether, ethyleneglycol diglycidyl ether, neopentylglycol diglycidyl ether, trimethylolpropane triglycidyl ether, glycerol triglycidyl ether, polypropyleneglycol diglycidyl ether, polyethyleneglycol diglycidyl ether, sorbitol polyglycidyl ether, N,N-diglycidylaniline, N,N-diglycidyltoluidine, N,N-diglycidyl-3-glycidoxyaniline, N,N-diglycidyl-2-glycidoxyaniline, bis(N,N-diglycidylamino)diphenylmethane, tris(2,3-epoxypropyl) isocyanurate, N,N-diglycidylbutylamine, and mixtures thereof.

The functionalized polymers are prepared by contacting one or more of the foregoing functionalizing agents, including mixtures thereof, with a pseudo-living polymer. If a solvent is employed, it is preferable to employ a solvent in which both the pseudo-living polymer and the functionalizing agent are soluble, or in which they may both be suspended. Preferably, this contacting takes place at a temperature of less than 160°C, and more preferably at a temperature from about 20°C to about 100°C. Further, the reaction time is preferably from about 0.1 to about 10 hours, and more preferably from about 0.2 to about 5 hours.

The amount of functionalizing agent used can vary. Preferably, from about 0.01 to about 200 moles of functionalizing agent per mole of lanthanide, and more preferably, from about 0.1 to about 150 moles per mole of lanthanide are employed.

The reaction between the pseudo-living polymer and the functionalizing agent is quenched by using reagents such as, but not limited to, isopropyl alcohol, methanol, and water. Stabilizers, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT), can be added during or after quenching.

Before quenching the resulting polymer, however, certain reactive compounds can be added to provide additional functionality to the polymer. These reactive compounds include those that will undergo addition reactions with metal alkoxides or metal amides. Addition of a protic quenching agent is believed to remove the metal via a substitution reaction and thereby leave a lanthanide or aluminum amino group at the polymer chain end. A reaction between the metal amide and the metal amide-reactive compound before quenching is believed to provide additional functionality.



The polymer product can be recovered by using any technique that is commonly employed in the art. For example, the polymer product can be coagulated in a hindered solvent such as isopropyl alcohol, and then dried in a hot air oven or hot mill. Alternatively, the polymer product can be recovered by steam desolventization and successive hot air drying or drying on a hot mill or the like. A processing oil can be added prior to finishing.

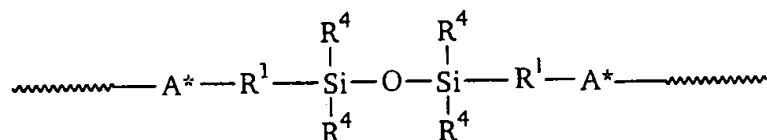
The resulting functionalized polymer can be represented by the formula (XV)



(XV)

where  $\text{R}^1$  and  $\text{R}^3$  are as defined above, and  $\text{A}^*$  is the residue of the imino portion of the functionalizing agent that has undergone an addition reaction with a pseudo-living polymer, and is polymer having a *cis* microstructure that is greater than about 85%, a 1,2- or 3,4- unit content that is less than about 3%, and a molecular weight distribution that is less than about 5. More preferably, the polymer has a *cis* microstructure that is greater than about 90%, a 1,2- or 3,4- unit content that is less than about 2%, and a molecular weight distribution that is less than about 4.

Polymers carrying alkoxysilane functionality may couple via a condensation reaction. For example, polymers represented by the formula (XV) may condense to form a coupled polymer that is represented by the following formula (XVI)



(XVI)

where A\*, R<sup>1</sup> and R<sup>4</sup> are as defined above.

Reference to the functionalized polymers will likewise include the condensation products thereof. In the event that any R<sup>4</sup> is OR<sup>5</sup>, it may likewise couple with another functionalized polymer. Advantageously, the coupling of  
5 functionalized polymers where Z is a silane group improves the cold flow resistance of the polymers.

The functionalized polymers of this invention can advantageously be used in the manufacture of various tire components including, but not limited to, tire treads, side walls, subreads, and bead fillers. They can be used as all or part  
10 of the elastomeric component of a tire stock. In one embodiment, the functionalized polymers comprise greater than about 10 percent by weight (pbw), more preferably, greater than about 20 pbw, and even more preferably greater than about 30 pbw, of the elastomeric component of the tire stock. Addition of the functionalized polymers to a tire stock does not alter the type or amount of other  
15 ingredients typically included within these vulcanizable compositions of matter. Accordingly, practice of this invention is not limited to any particular vulcanizable composition of matter or tire compounding stock.

Typically, tire stocks include an elastomeric component that is blended with reinforcing fillers and at least one vulcanizing agent. Accelerators, oils,  
20 waxes, fatty acids and processing aids are often included. Vulcanizable compositions of matter containing synthetic rubbers typically include antidegradants, processing oils, zinc oxide, optional tackifying resins, optional reinforcing resins, optional peptizers, and optional scorch inhibiting agents.

The functionalized polymers of this invention may be used in  
25 conjunction with other rubbers to form the elastomeric component of a tire stock. These other rubbers may include natural rubber, synthetic rubber, or both. Examples of synthetic rubber include synthetic poly(isoprene), poly(styrene-co-butadiene), poly(butadiene), poly(styrene-co-butadiene-co-isoprene) and mixtures thereof.

30 Reinforcing fillers may include both organic and inorganic fillers. Organic fillers include, but are not limited to carbon black, and inorganic fillers include, but are not limited to, silica, alumina, aluminum hydroxide, and

magnesium hydroxide. Reinforcing fillers are typically employed in an amount from about 1 to about 100 parts by weight per 100 parts by weight rubber (phr), and preferably from about 20 to about 80 parts by weight phr, and more preferably from about 40 to about 80 parts by weight phr based on the total weight of all reinforcing fillers employed. Typically, when an inorganic filler is used, it is used in combination with organic fillers. In these embodiments, the total amount of reinforcing filler will include from about 30 to about 99 parts by weight inorganic filler and 1 to about 70 parts by weight organic filler, based on 100 parts by weight total filler. More preferably, the total filler will include from about 50 to about 95 parts by weight inorganic filler and from about 5 to about 50 parts by weight organic filler based on 100 parts by weight filler.

Carbon blacks may include any commonly available carbon black, but those having a surface area (EMSA) of at least 20 m<sup>2</sup>/g, and more preferably at least 35 m<sup>2</sup>/g up to 200 m<sup>2</sup>/g or higher, are preferred. Surface area values used in this application are those determined by ASTM test D-1765 by using the cetyltrimethyl-ammonium bromide (CTAB) technique.

Silicas (silicon dioxide) are generally referred to as wet-process, hydrated silicas because they are produced by a chemical reaction in water, and precipitated as ultrafine, spherical particles. These particles strongly associate into aggregates that in turn combine less strongly into agglomerates. The surface area, as measured by the BET method, gives the best measure of the reinforcing character of different silicas. Useful silicas preferably have a surface area of about 32 to about 400 m<sup>2</sup>/g, preferably about 100 to about 250 m<sup>2</sup>/g, and more preferably about 150 to about 220 m<sup>2</sup>/g. The pH of the silica filler is generally about 5.5 to about 7 and preferably about 5.5 to about 6.8. Commercially available silicas include Hi-Sil<sup>TM</sup> 215, Hi-Sil<sup>TM</sup> 233, and Hi-Sil<sup>TM</sup> 190 (PPG Industries; Pittsburgh, Pennsylvania). Useful commercial grades of different silicas are also available from other sources including Rhone Poulenc.

Typically, a coupling agent is added when silica is used. One coupling agent conventionally used is bis-[3(triethoxysilyl) propyl]-tetrasulfide, which is commercially available under the tradename SI69 (Degussa, Inc.; New York, New York). Additional coupling agents may include bis(3-(triethoxysilyl)propyl)

trisulfide, bis(3-(triethoxysilyl)propyl) disulfide, 3-mercaptopropyltriethoxysilane, bis(3-(trimethoxysilyl)propyl) tetrasulfide, bis(3-(trimethoxysilyl)propyl) trisulfide, bis(3-(trimethoxysilyl)propyl) disulfide, 3-mercaptopropyltrimethoxysilane, 3-(trimethoxysilyl)propyl)diethylthiocarbamyl tetrasulfide, and 3-(trimethoxysilyl)propyl)benzothiazyl tetrasulfide. These agents are typically employed in an amount from about 1 to about 20 phr, and more preferably from about 3 to about 15 phr. Advantageously, less coupling agent is required when the functionalized polymers of this invention, which include a silane functionality, are employed.

Reinforced rubber compounds can be cured in a conventional manner with known vulcanizing agents. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer, *ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY*, 3<sup>rd</sup> Edition, Wiley Interscience, N.Y. 1982, Vol. 20, pp. 365-468, particularly VULCANIZATION AGENTS AND AUXILIARY MATERIALS pp. 390-402, or *Vulcanization* by A.Y. Coran, *ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING*, 2<sup>nd</sup> Edition, John Wiley & Sons, Inc., 1989. Vulcanizing agents may be used alone or in combination. This invention does not appreciably affect cure times. Typically, vulcanization is effected by heating the vulcanizable composition; e.g., it is heated to about 170°C. Cured or crosslinked polymers may be referred to as vulcanizates.

Tire formulations are compounded by using mixing equipment and procedures conventionally employed in the art. Preferably, an initial masterbatch is prepared that includes the elastomer component and the reinforcing fillers, as well as other optional additives such as processing oil and antioxidants. The polyolefin additives are preferably added during preparation of the initial masterbatch. Once this initial masterbatch is prepared, the vulcanizing agents are blended into the composition. The composition can then be processed into tire components according to ordinary tire manufacturing techniques including standard rubber curing techniques. Rubber compounding techniques and the additives employed therein are generally known as disclose in *The Compounding and Vulcanization of Rubber*, by Stevens in *RUBBER TECHNOLOGY SECOND EDITION* (1973 Van Nostrand Reinhold Company). Pneumatic tires can be made according

to U.S. Patent Nos. 5,866,171; 5,876,527; 5,931,211; and 5,971,046, which are incorporated herein by reference.

The functionalized polymers of this invention can also be used in the manufacture of hoses, belts, shoe soles, window seals, other seals, vibration  
5 damping rubber, and other industrial products.

In order to demonstrate the practice of the present invention, the following examples have been prepared and tested as described in the Examples Section disclosed hereinbelow. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

10

### EXAMPLES

A catalyst was prepared by mixing 0.45 g of 1,3-butadiene monomer in hexanes, 0.28 mmol of neodymium neodecanoate in hexanes, 27.5 mmol of methylaluminoxane in toluene, and 5.77 mmol of diisobutylaluminum hydride in  
15 hexanes within a dried and nitrogen purged bottle equipped with a rubber septum. After two minutes of contact, 1.10 mmol of diethylaluminum chloride in hexanes was added to the mixture. The mixture was then aged at room temperature for about 18 minutes.

Polybutadiene polymer was prepared by mixing the catalyst solution  
20 prepared above with 611 g of 1,3-butadiene monomer in about 3,460 g of hexanes at 27°C within a stainless steel reactor equipped with an agitator and a jacket to control temperature.

The functionalizing agents identified in Table I, each containing an imine reactive group, were added to the respective samples in an amount and at  
25 a temperature as set forth in Table I. The functionalizing agent was allowed to react for the time specified, quenched with a small amount of isopropyl alcohol and 2,6-t-butyl 4-methyl phenol (BHT) in hexanes, and then the polymer was isolated by coagulation in isopropyl alcohol and successive drum drying. Example 1, which was not functionalized with the imine functionalizing agent, was determined to  
30 have a 93 percent *cis* structure by using FTIR analysis.

Table I sets forth the Mooney Viscosity (ML 1+4 @ 100°C), the Mooney relaxation to 20% torque (T-80), the number average molecular weight ( $M_n$ ), the

weight average molecular weight ( $M_w$ ), and molecular weight distribution as determined by GPC analysis with universal calibration for polybutadiene based on polystyrene.

5 This mixture was agitated for about 8 minutes at 27°C, and then the jacket temperature was increased to 82°C and agitation continued for another 42 minutes, at which time the temperature was lowered to 70°C. Approximately 370 g of the polymer cement was sampled into seven separate dried and nitrogen-purged bottles, which are identified as Samples 1-9 in Table I. Polymer Sample 10 was obtained commercially under the tradename BR01™ (JSR Corp.; Tokyo, Japan).

TABLE I

Polymer Samples	1	2	3	4	5	6	7	8	9	10
Functionalizing Agent	None	DMAB-BPA	DMAB-BPA	DMAB-BPA	TEOSI	TEOSI	TEOSI	None	None	None
Amount of functionalizing agent (eq /Nd)	—	25	50	50	25	50	50	—	—	—
Reaction Temp (°C)	—	—	50	50	50	50	50	—	—	—
Reaction Time (min)	—	—	180	900	180	180	900	—	—	—
ML1+4 @ 100°C	44	48	48	49	74	57	63	32	55	43
T-80 (s)	4.0	4.0	4.0	4.0	5.3	4.3	5.1	3.3	4.0	8.5
Mn (kg/mol)	140	141	140	135	144	133	141	122	146	77
Mw (kg/mol)	274	274	277	280	294	277	277	240	307	306
Mw/Mn	2.0	1.9	2.0	2.1	2.0	2.1	2.0	1.97	2.09	4.0
% functionality	0.0	62.8	60.7	58.7	N/A	N/A	N/A	0	0	0

Sample polymers 4, 7, 8, 9, and 10 were individually compounded into rubber formulations with carbon black (N339) as a filler. Samples 1,3,and 6 were individually compounded into rubber formulations with silica (Nipsil VN3™; Nippon Silica; Japan). An initial masterbatch was blended within an internal mixer at an initial temperature of about 110°C for about 3.5 minutes. The masterbatch was allowed to cool and then re-milled within the same internal mixer for about 2 minutes. Then, a cure system was added while the compound was continually processed within the internal mixer at a temperature of about 80°C for about 1 minute. The compounding recipes that were employed are set forth in Tables II and III.

**TABLE II**  
**COMPOUNDING RECIPE WITH CARBON BLACK**

	<b>Ingredient</b>	<b>Parts per Hundred Rubber</b>
15	Elastomer	100
	Aromatic Oil	10
	Paraffin Oil	1.5
	Carbon Black	50
	Stearic Acid	2
20	Antioxidant	1
	Masterbatch Total	164.5
	Zinc Oxide	2
	Sulfur	1.3
25	Accelerators	1.2
	Total	169.0



TABLE III

## COMPOUNDING RECIPE WITH SILICA

Ingredient	Parts per Hundred Rubber
Elastomer	100
Aromatic Oil	10
Silica	50
Stearic Acid	2
Antioxidant	1
Masterbatch Total	163
Zinc Oxide	2.5
Sulfur	.03
Accelerators	2.5
Total	171.5

Once compounded, each formulation was press cured at about 145°C for about 33 minutes. The cured samples were then analyzed to determine tensile strength at break, moduli, and elongation at break according to JIS-K6301. Bound rubber was measured by immersing finely shredded uncured rubber specimens into toluene at room temperature. After 40 hours, the composition was filtered and bound rubber was calculated from the weight of the dried sample compared to other insoluble ingredients. Also, the samples were tested to determine  $\tan \delta$  at 50°C (frequency at 31.4 rad/s and 3% strain).

The percent functionality of the polymer was obtained from the area ratios of UB and RI chromatograms and the number average molecular weight of the polymer ( $M_n$ ) obtained by GPC by using universal calibration for polystyrene and high *cis* butadiene based on polystyrene standards. The following three assumptions were made: (1) the UV absorbance of an end-functional group on a *n*-butyllithium (*n*-BuLi) initiated polymer was the same as the UV absorbance of the end-functional group on a lanthanide-catalyzed polymer, (2) *n*-BuLi initiated

polymers are 100% functionalized, and (3) the area ratio of UV/RI is a linear function of the inverse of the  $M_n$  of the polymer. Pursuant to the method employed, a calibration curve of UV/RI area ratio (A) and  $M_n$  of polymers that were initiated with *n*-BuLi and terminated with the same imine compound was established according to the following formula:  $A = a(1/M_n) + b$  where  $A_{(\text{BuLi, endgroup})} = A_{(\text{BuLi, polymer})} - A_{(\text{BuLi-backbone})} = (a_{(\text{polymer})} - a_{(\text{backbone})})(1/M_n) + (b_{(\text{polymer})} - b_{(\text{backbone})})$ . Parameters *a* and *b* were obtained by least square linear fitting of GPC data of *n*-BuLi initiated and imine terminated polymers and *n*-BuLi initiated and alcohol terminated polymers, with 3 different molecular weights. The percent functionalities (F) of unknown polymers initiated by lanthanide catalysts were obtained from GPC data of the functionalized, unknown polymer and the corresponding unfunctionalized (base) polymer according to the following formula:  $F = A_{(\text{unknown, endgroup, M})} / A_{(\text{BuLi, endgroup, M})} = (A_{(\text{unknown, polymer, M})} - A_{(\text{unknown, backbone, M})}) / [(a_{(\text{polymer})} - a_{(\text{backbone})})(1/M) + (b_{(\text{polymer})} - b_{(\text{backbone})})]$ .

The results of testing the vulcanizates filled with carbon black are set forth in Table IV, and the results of testing the vulcanizates filled with silica are set forth in Table V. The data in Table IV, except for Mooney Viscosity (ML1+4@100°C), has been indexed to the vulcanizates prepared by using polymer Sample 10, and the data in Table V, except for Mooney Viscosity, has been indexed to the vulcanizates prepared by using polymer Sample 1. The polymer sample labeled A is a weighted average between sample polymers 8 and 9 calculated to provide Mooney Viscosity (ML1+4@100°C) of about 44.

TABLE IV

Polymer Samples	4	7	8	9	10	A
ML1+4 @ 100 °C	49	63	32	55	43	44
Bound Rubber (index)	80	132	61	73	100	67
Tan $\delta$ at 50 °C (index)	125	131	110	132	100	120
Tensile Strength at Break at 23 °C (MPa) (index)	101	87	107	109	100	108
300% Modulus at 23 °C (MPa) (index)	103	120	103	118	100	111
Elongation at Break at 23 °C (%) (index)	96	79	101	93	100	97
Tensile Strength at Break at 100 °C (MPa) (index)	79	97	91	87	100	89
300% Modulus at 100 °C (MPa) (index)	101	120	104	109	100	106
Tensile Strength at Break at 100 °C (MPa) (index)	80	83	90	82	100	86

TABLE IV CONTINUED

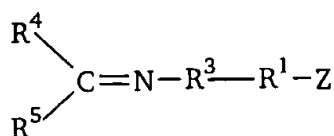
Polymer Samples	1	3	6
ML1+4 @ 100 °C	44	48	57
Bound Rubber (index)	100	230	593
Tan $\delta$ at 50 °C (index)	100	112	125
Tensile Strength at Break at 23 °C (MPa) (index)	100	112	69
300% Modulus at 23 °C (MPa) (index)	100	107	116
Elongation at Break at 23 °C (%) (index)	100	102	73
Tensile Strength at Break at 100 °C (MPa) (index)	100	98	52
300% Modulus at 100 °C (MPa) (index)	100	116	n/a
Tensile Strength at Break at 100 °C (MPa) (index)	100	86	42

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

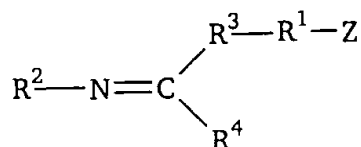
## CLAIMS

What is claimed is:

- 1 1. A method for preparing a functionalized polymer comprising the steps of:  
 2 preparing a pseudo-living polymer by polymerizing conjugated diene  
 3 monomer with a lanthanide-based catalyst; and  
 4 reacting the pseudo-living polymer with at least one functionalizing  
 5 agent defined by the formula (I) or (II)



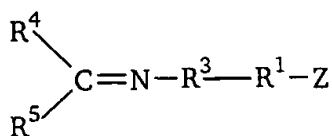
(I)



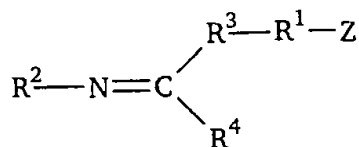
(II)

12 where Z is a substituent that will react or interact with organic or inorganic  
 13 fillers; R<sup>1</sup> is a single bond or a divalent organic group; R<sup>2</sup> is a monovalent  
 14 organic group or a divalent organic group that forms a cyclic organic group  
 15 with R<sup>3</sup> or R<sup>4</sup>; R<sup>3</sup> is a single bond, a divalent organic group, or a trivalent  
 16 organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup>; R<sup>4</sup> is a  
 17 monovalent organic group or a divalent organic group that forms a cyclic  
 18 organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>5</sup>; R<sup>5</sup> is a monovalent organic group or a  
 19 divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup>;  
 20 with the proviso that each group attached to the imino carbon is attached via  
 21 a carbon atom and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Z are substituents that will not  
 22 protonate a pseudo-living polymer.

- 1 2. A functionalized polymer prepared by a process comprising the steps of:  
 2 preparing a pseudo-living polymer by polymerizing conjugated monomer  
 3 with a lanthanide-based catalyst; and  
 4 reacting the pseudo-living polymer with a functionalizing agent defined  
 5 by the formula (I) or (II)



(I)

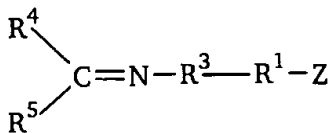


(II)

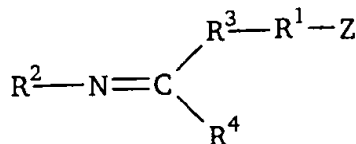
where Z is a substituent that will react or interact with organic or inorganic fillers; R<sup>1</sup> is a single bond or a divalent organic group; R<sup>2</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>3</sup> or R<sup>4</sup>; R<sup>3</sup> is a single bond, a divalent organic group, or a trivalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup>; R<sup>4</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>5</sup>; R<sup>5</sup> is a monovalent organic group or a divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup>; with the proviso that each group attached to the imino carbon is attached via a carbon atom and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Z are substituents that will not protonate a pseudo-living polymer.

3. A vulcanizable composition of matter comprising:

- (a) a rubber component comprising a functionalized polymer prepared by a process comprising the steps of
  - preparing a pseudo-living polymer by polymerizing conjugated monomer with a lanthanide-based catalyst; and
  - reacting the pseudo-living polymer with a functionalizing agent defined by the formula (I) or (II)



(I)



(II)

14           where Z is a substituent that will react or interact with organic or  
15           inorganic fillers; R<sup>1</sup> is a single bond or a divalent organic group; R<sup>2</sup> is  
16           a monovalent organic group or a divalent organic group that forms a  
17           cyclic organic group with R<sup>3</sup> or R<sup>4</sup>; R<sup>3</sup> is a single bond, a divalent  
18           organic group, or a trivalent organic group that forms a cyclic organic  
19           group with R<sup>2</sup>, R<sup>4</sup>, or R<sup>5</sup>; R<sup>4</sup> is a monovalent organic group or a  
20           divalent organic group that forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or  
21           R<sup>5</sup>; R<sup>5</sup> is a monovalent organic group or a divalent organic group that  
22           forms a cyclic organic group with R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup>; with the proviso that  
23           each group attached to the imino carbon is attached via a carbon atom  
24           and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and Z are substituents that will not protonate a  
25           pseudo-living polymer; and  
26           (b) a reinforcing filler.

1     4.   The method of claim 1, polymer of claim 2, or vulcanizable composition of  
2     claim 3, where the pseudo-living polymer includes greater than about 85 percent  
3     by weight polymeric units in the *cis* microstructure and less than about 3 percent  
4     by weight polymeric units in the 1,2- or 3,4- microstructure, and where the pseudo-  
5     living polymer has a molecular weight distribution that is less than about 4.

1     5.   The method, polymer, or vulcanizable composition of claim 4, where the  
2     pseudo-living polymer is poly(butadiene).

1     6.   The method of claim 1, polymer of claim 2, or vulcanizable composition of  
2     claim 3, where Z is a silane group, an N,N-disubstituted amino phenyl group, an  
3     imine group, or a cyclic amino group.

1     7.   The method of claim 1, where the functionalizing agent comprises N-(3-  
2     triethoxysilylpropyl)-4,5-dihydroimidazole, N-(1,3-dimethylbutylidene)-3-  
3     triethoxysilyl)-1-propaneamine, oligomers thereof, or mixtures thereof;  
4     dimethylaminobenzylidene ethylamine, diethylaminobenzylidene butylamine;



5 dimethylaminobenzylidene aniline, dimethylaminobenzylidene n-butylaniline,  
6 dimethylaminobenzylidene dodecylaniline, dimethylaminobenzylidene  
7 methoxyaniline, dimethylaminobenzylidene dimethylaminoaniline;  
8 bis(dimethylaminophenyl)methylidene butylamine,  
9 bis(dimethylaminophenyl)methylidene n-octylamine,  
10 bis(diethylaminophenyl)methylidene butylamine,  
11 bis(diethylaminophenyl)methylidene n-octylamine, benzylidene  
12 dimethylaminoaniline, methoxybenzylidene dimethylaminoaniline, 1-methyl-4-  
13 pentene-2-yl-methylidene dimethylaniline, 1,3-dimethylbutylidene dimethylaniline,  
14 or mixtures thereof; phenylene bis(dimethylaminobenzylidene amine); benzylidene  
15 (1-hexamethyleneimino)aniline, benzylidene (1-pyrolidino)aniline,  
16 dimethylaminobenzylidene (1-hexamethyleneimino)aniline,  
17 dimethylaminobenzylidene (1-pyrolidino)aniline, (1-  
18 hexamethyleneimino)benzylidene aniline, (1-pyrolidino)benzylidene aniline,  
19 benzylidene ((4-n-butyl-1-piperazino)methyl)aniline, benzylidene ((3-(1-  
20 methyl)pyrolidino)methyl)aniline, ((4-n-butyl-1-piperazino)methyl)benzylidene  
21 aniline, ((3-(1-methyl)pyrolidino)methyl)benzylidene aniline, or mixtures thereof.

1 8. The method of claim 1, polymer of claim 2, or vulcanizable composition of  
2 claim 3, where the functionalizing agent is present in an amount of from about  
3 0.01 to about 200 moles of functionalizing agent per mole of lanthanide-based  
4 catalyst.

1 9. The vulcanizable composition of claim 3, where the inorganic filler comprises  
2 silica.

1 10. A tire tread prepared from the vulcanizable composition of claim 3.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/30875

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08C19/44 C08L19/00 C08F136/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08C C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 310 798 A (LAWSON DAVID F ET AL) 10 May 1994 (1994-05-10)	2,4-8
Y	abstract column 5, line 20 - line 53 column 6, line 50 - line 60 column 7, line 43 - line 54 column 9, line 21 - line 39 examples 5,6 claims 1-6 --- -/--	1,3-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*g\* document member of the same patent family

Date of the actual completion of the international search

1 February 2001

Date of mailing of the international search report

26/02/2001

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/30875

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>EP 0 882 738 A (NIPPON ZEON CO)            9 December 1998 (1998-12-09)            abstract            page 5, line 4 - line 17            page 6, line 54 - line 56            page 8, line 21 - line 41            tables 4,5            claims 1-9</p> <p style="text-align: center;">-----</p>	1,3-10

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/30875

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5310798 A	10-05-1994	CA 2130144 A DE 69406385 D DE 69406385 T EP 0639587 A ES 2109567 T JP 7149825 A	17-02-1995 27-11-1997 26-02-1998 22-02-1995 16-01-1998 13-06-1995
EP 0882738 A	09-12-1998	JP 9227628 A US 6147178 A WO 9731028 A	02-09-1997 14-11-2000 28-08-1997